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**POST-HARVEST PROCESSING METHODS FOR REDUCTION OF
SILICA AND ALKALI METALS IN WHEAT STRAW**

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SUMMARY

Silica and alkali metals in wheat straw limit its use for bioenergy and gasification. Slag deposits occur via the eutectic melting of SiO_2 with K_2O , trapping chlorides at surfaces and causing corrosion. A minimum melting point of 950°C is desirable, corresponding to $\text{SiO}_2:\text{K}_2\text{O}$ of about 3:1. Mild chemical treatments were used to reduce Si, K, and Cl, while varying temperature, concentration, %-solids, and time. Dilute acid was more effective at removing K and Cl, while dilute alkali was more effective for Si. Reduction of minerals in this manner may prove economical for increasing utilization of the straw for combustion or gasification.

KEYWORDS: Bioenergy, combustion, gasification, fluidized bed, silica, potassium, chloride, slagging

INTRODUCTION

Agricultural crop residues are a valuable renewable resource from which to produce biobased products. In 1999, American farmers harvested 53,909,000 acres of wheat (1). The straw from this acreage of wheat represents over 100 million tons annually. Currently, some of the straw is harvested (baled) for use as livestock bedding or low-grade animal feed. However, these low-value uses provide only a minimal return. Nationally, only about 3.2% of the economic return on wheat is from straw (1). Producers have long recognized the potential economic and environmental benefits in producing bioenergy and bioproducts from excess wheat straw residue. However, the silica and alkali metals in wheat straw limit its use for bioenergy and gasification.

Because of slagging, fluidized bed combustors and gasifiers cannot be operated above the ash fusion temperature of the feedstock, and boilers can only be operated well above or well below the ash fusion temperature (2). Wheat straw contains significant amounts of low-melting ash, which is comprised

of mineral oxides including primarily SiO_2 , K_2O , and CaO , with smaller amounts of SO_3 , MgO , Na_2O , Fe_2O_3 , Al_2O_3 , and TiO_2 (3). This mineral ash deposits onto furnace or heat transfer surfaces in two ways. “Slagging” is deposition of molten or highly viscous ash, and occurs in the hottest regions of the combustor or gasifier. In contrast, “fouling” is deposition by condensation of vaporized ash, and occurs in the cooler regions. Vaporized KCl is then held in close contact with the metal surfaces of the combustor or gasifier, causing corrosion. Ash fusibility is an important factor in determining whether slagging or fouling will occur. K_2O and other oxides form a eutectic mixture with SiO_2 , lowering the ash fusion temperature (4). K_2O is of particular importance in the slagging of biomass ash due to its high concentration. For comparison, pure SiO_2 melts at $1703\text{ }^\circ\text{C}$ (5), while a 4:1 $\text{SiO}_2/\text{K}_2\text{O}$ mixture by wt melts at about $1100\text{ }^\circ\text{C}$, a 3:1 mixture melts at about $950\text{ }^\circ\text{C}$, and a 2.3:1 mixture melts at about $850\text{ }^\circ\text{C}$ (6) (i.e. lower $\text{SiO}_2/\text{K}_2\text{O}$ ratios lead to lower ash fusion temperatures). While an efficient operating temperature is about $1100\text{ }^\circ\text{C}$, the preferred minimum is about $950\text{ }^\circ\text{C}$ depending on the design (6). Thus, an effective treatment to remove minerals from straw reducing slagging and corrosion during combustion or gasification will: (1) Reduce total SiO_2 content; (2) Increase $\text{SiO}_2/\text{Alkaline oxide}$ ratios, particularly $\text{SiO}_2/\text{K}_2\text{O}$; and (3) Increase the SiO_2/KCl ratio.

The cellulose-rich vascular tissues of straw stems contain relatively higher amounts of organic material and fermentable carbohydrates for conversion to bioenergy, biofuels and chemicals. In contrast, the formerly physiologically active tissues, including the leaves, sheaths and awns, are heavily impregnated with silica in the epidermal layer, and these tissues also contain higher amounts of non-carbohydrate organic components (i.e., protein, lipids, pigments, pectin, organic acids) than the stems. For cost-efficient utilization of straw and other crop residues for bioenergy or gasification, the undesirable mineral components must be removed. However, the current paradigm for straw utilization includes the necessity to transport all the components of the straw to the point of use. There is no cost-efficient way to remove undesirable components from straw before transportation. This is expensive not only because of the low bulk density of straw, but also because it brings the less valuable components to the manufacturer’s gate and creates economic and environmental liabilities.

In this paper, we describe tests conducted at the Idaho National Engineering and Environmental Laboratory (INEEL) to further reduce silica and alkali mineral loads in the straw stem fraction to allow its use for bioenergy production and gasification in fluidized beds and boilers. The objectives of this study were: (1) Reduce SiO₂ content to minimize total slag formation; (2) Reduce K₂O, increasing the ratio of SiO₂ to alkaline oxides and increasing the temperature at which the slag forms; (3) Remove chlorides, minimizing the potential for corrosion due to the generation of KCl vapor at metal surfaces beneath slagging and fouling deposits; and (4) Perform these reductions in a manner that can be used economically in both distributed and centralized systems.

METHODS

Wheat Straw. Westbred 936 wheat straw, a hard red spring variety, was obtained from Grant 4-D Farms (Rupert, ID). All straw utilized in the laboratory studies was produced during the year 2000 cropping season. Twenty large bales of Westbred 936 (1.2 m × 2.4 m bales (4 ft × 8 ft)) were collected and stored in a stack at the side of the field, using only the protected center bales for the studies. To better handle the straw for the laboratory studies, the large bales were rebaled as needed into smaller 0.61 m × 1.2 m (2 ft × 4 ft) bales containing about 22.7 kg (50 lb) each, and stored in covered storage. The straw was rethreshed before use in the mineral removal studies as described by Hess *et al.* (7), to remove the high-silica plant components including the leaves, sheaths, fines, and nodes. Only the separated straw stems were used in the laboratory studies.

Chemical wash procedure. Five to twenty grams of air-dried whole chopped straw or mechanically-separated straw stems were weighed to the nearest 0.1 mg into a tared 500-mL wide-mouth polypropylene, Teflon, or polycarbonate bottle. Sufficient wash solution was weighed into the bottle to achieve the desired solids-% for the experiment (4-16 wt%). Wash solutions included distilled (DI) water, 0.1-5.0 wt% H₂SO₄, or 0.1-1.0 wt% NaOH. The bottles were shaken at a minimum of 150 rpm for 0.5-24 hours at the desired temperature (25, 37 or 50°C). The liquid was then poured off into tared Pyrex beakers. The straw stems were washed quickly with about 25 mL of distilled water, which was added to the collected liquid. Both the collected liquid fraction and the treated stems were then dried at 90-105°C

for at least 2 days. The dried samples were removed from oven, cooled, and their weights recorded. The dried straw samples were then ground to 60 mesh in a Wiley mill and stored at room temperature for carbohydrate, lignin, ash, and mineral analyses.

Analytical methods.

Ashing. At least 1 gram of dry straw, ground to 60 mesh, was weighed to the nearest 0.1 mg into a dry, tared ceramic crucible. The residue from the collected liquid fraction was also dried and weighed. Ashing was done in a muffle furnace at 550-650 °C for 18-24 hours. On selected samples, a duplicate or spike such as SiO₂ flour or potassium silicate was added to the straw before ashing to validate silica measurements. Ashing temperatures as high as 940 °C were used to determine weight loss as a function of temperature and composition changes from the volatilization of KCl.

Mineral analyses.

Energy Dispersive Spectrometry. Mineral analyses were done by Energy Dispersive Spectrometry (EDS), modifying existing geological and metallurgical procedures (8). The spectra were measured at 10-20 KeV using a Phillips XL30ESEM Scanning Electron Microscope with a Princeton Gamma Tech Detector (Princeton, NJ). Compositions of minerals in the ash were determined for the elements Si, K, Ca, S, Mg, Mn, Ti, Fe, Al, P, Na, Cl, O. Except for some carbon that remains after the ashing and some losses of KCl these elements should account for >95% of the ash. Ashed straw was placed in a thin film onto an aluminum disk using double-sided tape, taking care to transfer as much ash as possible onto the taped disk. The disks were then carbon-coated to prevent charging. Two or three separate 1.0 mm² areas of each disk were scanned to verify homogeneity, depending on whether the measured Si values differed by more than one percent among measurements. Scanning was done for 5-10 minutes, with longer times used for samples containing very small distinguishable peaks.

EDS standards, prepared from reagent grade silicates, oxides, and chlorides, and ashed at the same temperatures used for the samples, were used to prepare calibration curves to correct the internal quantitative EDS values for matrix effects. In addition, Standard Reference Materials, including coal fly

ash (SRM #1633 and #2690) and soil (SRM #2710), both from the National Institute of Standards and Technology (Gaithersburg, MD), were also used to check the accuracy of the instrument and the quantification software. Finally some straw samples were analyzed by Inductively-Coupled Plasma (ICP) analysis (9) to validate the EDS results. Oxide compositions were calculated from the elements based on standard stoichiometric ratios.

Inductively-Coupled Plasma. Mineral analysis by ICP (9) was done to validate EDS results (> 1 wt% K and Ca, < 1 wt% P, K, S, Mg, Fe) and quantify trace elements (< 0.1 wt%), particularly the composition of straw micro-nutrients in the ash, such as Cu, Zn, Mn and B. Straw samples and standard reference material / calibration standards used for the EDS analyses were shipped to Western Labs (Parma, ID) for ICP analyses. Western Labs measured P, Ca, K, Cu, Zn, B, Fe, and Mn using standard methods (10).

Carbohydrate and lignin analysis. Carbohydrate and lignin compositions of untreated and treated straw samples were determined by quantitative saccharification using the method of Saeman *et al.* (11). Carbohydrate analyses were done by high performance liquid chromatography (HPLC) using a BioRad HPX-87P carbohydrate column, and lignin was calculated by weight difference as Klason lignin with extractives and ash.

RESULTS AND DISCUSSION

The organic and ash compositions of the untreated baled straw and untreated mechanically separated straw stem fraction are shown in Table 1. Mechanical separation reduced the total ash and SiO₂ concentrations of the harvested fraction by 23% and 44%, respectively, thereby reducing overall slagging potential (7). However, mechanical separation concentrated the alkali metals relative to SiO₂, reducing the SiO₂/K₂O and SiO₂/KCl ratios. Although reduction of total SiO₂ is important for overall reduction of potential slag formation, in terms of modifying the eutectic properties and thereby raising the ash fusion temperature, removal of SiO₂ is detrimental without also removing proportional amounts of K, since it decreases the SiO₂/K₂O ratio in the ash.

Washing straw with aqueous liquids removed both organic and mineral matter. Most of the

removal occurred in the first 4 hours of washing. The ratio of organic losses to inorganic losses were similar with all of the wash solutions; that is, no particular wash solution was more selective for dissolution of organic components or minerals. Rather, the minerals appeared to be released along with organic material, such that very short or very long washes released approximately the same ratio of organic and inorganic components of the straw.

Three wash solutions, including distilled (DI) water, dilute H_2SO_4 , and dilute NaOH , were used separately to remove minerals from separated stems and from chopped whole straw. A general comparison of the effects of these washes on $\text{SiO}_2/\text{K}_2\text{O}$, SiO_2/KCl , and the loss of heating value, at 25, 37, and 50°C is shown in Figures 1 – 3. Acid washing of straw removed most of the potassium by dissolution, and gave the highest $\text{SiO}_2/\text{K}_2\text{O}$ ratios. Some acid washes removed sufficient potassium to raise the $\text{SiO}_2/\text{K}_2\text{O}$ ratio above the desired minimum ratio of 3.0. The highest removal of K and Cl in straw stems occurred with an 0.2 wt% acid wash at 50°C (Figure 1). This acid wash increased the $\text{SiO}_2/\text{K}_2\text{O}$ ratio from 0.9 to 3.2, and increased the SiO_2/KCl ratio from 0.5 to 71.3 (Figure 2), significantly reducing corrosion potential. For this calculation, it was assumed that all chlorine was present as KCl. The concentration of SiO_2 in the DI water- and acid-washed stems remained constant even though other mass was lost. Thus, both water and acid removed some SiO_2 but its removal was offset by the removal of organic matter, and the concentration in the washed stems remained the same. Alkaline washing dissolved up to 20% of the SiO_2 and slightly lowered the final SiO_2 concentration in the straw. However, the $\text{SiO}_2/\text{K}_2\text{O}$ ratio was lowered because a proportional amount of potassium was not removed.

The effect of wash solution and temperature on loss of heating value is shown in Figure 3. For these calculations, all components of the organic matter were assumed to be of equal heating value per unit weight. In general, higher wash temperatures resulted in greater loss of mass in acid washes, with smaller increases in the base and water washes. Increases in acid concentration increased the amount of mineral removed, but did so at the expense of BTU content since organic matter was also removed; about 80% of the mass removed in the acid washes was organic (not shown). These losses, amounting to 6-

11%, indicate that there is a trade-off between the cost of the lost heating value and the benefits of reducing minerals through use of the treatment.

The effects of chemical washing of straw on the organic component mass balances are shown for selected experiments in Figures 4-7, while the $\text{SiO}_2/\text{K}_2\text{O}$, SiO_2/KCl , and percentage of the ash represented by SiO_2 , K_2O , and KCl are given in Table 2. Figure 4 shows a comparison of a 24h, 15 wt%-solids wash and a 4h, 16 wt%-solids wash of straw stems. Note that DI water is a slightly more aggressive solvent than tap water because it has been demineralized; thus, the DI water washes indicate the maximum removals possible using water. Equilibrium was reached by 4 hours in all washes. The effect of percentage solids (solids loading) in the DI water washes is also shown in Figure 4. Increasing the %-solids resulted in decreased removal of both organic matter and minerals. This occurred whether the straw remained immersed in the bulk liquid, or was only partly immersed (15 %-solids). This indicates that the process is solubility limited as long as the straw is submerged, and may become liquid-solid contact-limited at solids loadings as high as 15 %-solids.

It was also observed that the differences between mineral removal at low and elevated temperatures (37 and 50 °C; not shown) was not as great at higher mass loadings, since solubility limits the amount of material that can be dissolved rather than the more aggressive solvent characteristics secured at the higher temperature. Washing with water removed 11.1% of the mass of straw in a 4% fully-submerged suspension, while only 6.8 % mass was removed in a 15% partially-submerged suspension. The ash concentration of unwashed straw was reduced to 4.6% in the 4%-solids water wash, but to only 6.7% in the 15%-solids wash. A continuous wash that lowers the effective “loading” even further would overcome the solubility limitations and may result in higher mineral losses than experienced in these batch experiments. However, acidic or alkaline washing in a continuous process may present some difficulty in removing the residual wash fluid from the straw if residual SO_4 or Na is not desirable. In the specific case of Na , this would definitely not be desirable, since both Na and K contribute to the eutectic composition and lower the ash fusion temperature. The straw stems absorbed about 3.7 times their weight of water, and chopped whole straw absorbed 4.2 times its weight. Thus,

residual SO_4 or Na might be difficult to remove efficiently without significant further water washes.

Mass balances for washing of straw stems at 25 °C with dilute acid at various acid concentrations are shown in Figure 5, while Figure 6 shows the same for whole straw at 50 °C. Higher acid concentrations were required to reach the same $\text{SiO}_2/\text{K}_2\text{O}$ ratios for whole straw as reached for stems at 50 °C (not shown). Still, $\text{SiO}_2/\text{K}_2\text{O}$ ratios obtained with whole straw approached the minimum acceptable level of 3.0. However, the whole straw contains larger amounts of silica (separated from the stem fraction in the selective harvest), and therefore greater slagging potential. Both the mineral and organic content removed increased with higher acid concentrations. The highest K removal without excessive loss of organic matter was achieved at 50 °C with 0.2 wt% H_2SO_4 in a 4% straw suspension (see Figure 2 above). The $\text{SiO}_2/\text{K}_2\text{O}$ ratio achieved in this run was approached with whole straw ($\text{SiO}_2/\text{K}_2\text{O}$ of 2.8) at 10 %-solids, which was not achievable with stems alone at 10 %-solids. This may be because the whole straw starts at a higher $\text{SiO}_2/\text{K}_2\text{O}$ ratio than stems alone, since the mechanical stem separation concentrated the alkali metals relative to the silica in the stems. In any event, lowering the solids content would probably produce washed straw with a $\text{SiO}_2/\text{K}_2\text{O}$ ratio above the desired minimum of 3.0.

Generally cellulose and hemicellulose concentrations were not significantly affected by dilute acid washes with acid concentrations up to 0.4%. However, Figure 5 shows significant loss of hemicellulose in a 1 % H_2SO_4 wash. A 5 % H_2SO_4 wash (not shown) resulted in complete loss of both cellulose and hemicellulose. In these experiments, the mass balances indicated a shift from cellulose and hemicellulose to an acid insoluble fraction, generally referred to as Klason lignin in the quantitative saccharification technique (11). It is believed that significant H_2SO_4 remained within the straw lignocellulosic matrix during the 105 °C drying step. Thus as water was removed, the H_2SO_4 was concentrated, eventually reacting with the polysaccharides at the elevated temperature and converting them to acid-insoluble organic matter. Assuming that the acid-insoluble organic was still combustible, the total BTU content may not be significantly affected, since the decomposition products were not lost, but converted to the “lignin” category in Figure 5. Hence, it is clear that acid concentrations of 1 wt%

and higher should not be used if recovery of intact carbohydrates is desired.

The effect of size reduction is demonstrated in Figure 6. As this chopped ($\frac{3}{4}$ inch and smaller fragments) straw had not been physically separated, the initial mineral (ash) content was higher at 11.2%. Size reduction increased the contact surface area and the mass that could be fully immersed. Ash removal upon washing was not improved, indicating solubility constraints were of greater importance than surface contact. The chopped whole straw was washed in water and various dilute H_2SO_4 solutions at 6.7 and 10 wt% solids. The mass lost after washing was 14.1% for the chopped straw at 6.7% loading. This was comparable to previous tests where 15.3% loss for straw stems at 4.5% loading was observed. The inorganic mineral concentration was reduced from 11.2 to 6.4% in the chopped whole straw, and from 8.7 to 4.2% in the unchopped straw stems.

It seems clear from the data presented in this paper that acid is preferred as a wash solution for removal of alkali minerals from straw for use in fluidized bed combustors or gasifiers or in boilers. Future work includes testing acid-washed whole straw and physically separated straw stems in a fluidized bed combustor to determine the combustion and slagging properties of the washed straw. In addition, we would like to test the effect of adding CaO or MgO after washing, since CaO and MgO can modify the eutectic composition and thereby increase the ash fusion temperature further (2). While CaO or MgO could be directly added to the straw without washing to achieve an increase in ash fusion temperature, washing the straw removes large amounts of potassium and thus less CaO and MgO would be required to significantly alter the ash fusion temperature. Data from these tests, and estimation of eutectic compositions and ash fusion temperatures, will help in the application of these separations to fluidized bed combustion and gasification of biomass and combustion in boilers. The acid-washed straw will also be tested for ease of drying and densification as part of a distributed bioenergy system.

CONCLUSIONS

Mechanical separation of straw reduced ash and SiO_2 concentration in straw by removing leaves and sheaths and leaving primarily stems. However this concentrated K relative to SiO_2 , reducing the SiO_2/K_2O and SiO_2/KCl ratios, which are important measures of slagging and corrosion potential.

Chemical washes removed much of the soluble K and up to 11% organic matter. Dilute acid removed both K and Cl while dilute base removed limited amounts of SiO₂. Elevated temperatures increased both mineral removal rate, and with sufficient bulk liquid, the amount removed. The highest SiO₂/K₂O ratio achieved was 3.2, using a 4h wash in 0.2 wt% H₂SO₄ at 50°C, using a 4% straw stem suspension. Increasing the solids loading minimized loss of organics, but also reduced mineral removal. Washing improved SiO₂/K₂O and SiO₂/KCl ratios for both physically separated straw stems and whole straw.

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FIGURE LEGENDS

Figure 1: SiO₂/K₂O ratio after acid, alkali, or water washing of straw stems at various temperatures.

Figure 2: SiO₂/KCl ratio after acid, alkali, or water washing of straw stems at various temperatures.

Figure 3: Loss of heating value as a function of acid, alkali, and water washing of straw stems at various temperatures.

Figure 4: Mass balances for unwashed straw stems and for washed straw stems using DI water at 25°C for 4 or 24h, with increasing %-solids.

Figure 5: Mass balances for unwashed straw stems and for washed straw stems using dilute H₂SO₄ at 25°C for 4h, at 4 %-solids, with increasing acid concentration.

Figure 6: Mass balances for unwashed whole chopped straw and for washing of whole chopped straw using dilute H₂SO₄ at 50°C for 24h, at 10 %-solids, with increasing acid concentration.

TABLES

Table 1: Organic and Inorganic Composition of whole Westbred 936 straw and the mechanically-separated straw stem fraction.

Component	Wt% of Component ^a in	
	Westbred 936 Whole straw	Westbred 936 Stems only
Glucan	32.1	37.2
Xylan	19.3	19.4
Galactan	1.0	0.9
Mannan	4.5	3.0
Arabinan	2.1	1.6
Lignin with Extractives	20.3	18.9
Other ^c	9.5	10.3
Ash ^b wt%	11.2	8.7
SiO ₂	2.6	1.3
K ₂ O ^d	1.7	1.2
KCl ^d	5.2	5.2
CaO	0.6	0.2
SO ₃	0.4	0.3
MgO	0.3	0.2
P ₂ O ₅	0.2	0.1
FeO	0.04	0.05
Na ₂ O	0.06	0.04
MnO ₂	0.005	0.003
CuO	0.0005	0.0005
B ₂ O ₃	0.005	0.005
Al ₂ O ₃	0.0002	<0.005
TiO ₂	<0.005	0.0001
ZnO	0.0007	0.004
SUM	100	100

a. Based on 100% dry weight of material

b. Oxide contents estimated by mass balance from elemental composition as determined by EDS

c. Other organics are attributed to uronic acid, protein, etc. contents and to recovery errors in carbohydrate analysis technique.

d. Potassium assumed to first combine with available chlorine then apportioned as oxide

Table 2: SiO₂/K₂O, SiO₂/KCl, and percentage of the ash represented by SiO₂, K₂O, and KCl for the washes shown in Figures 4-6.

Condition	SiO ₂ /K ₂ O	SiO ₂ /KCl	wt% SiO ₂ , K ₂ O, & KCl
<i>4-24h, 25 °C, stems, H₂O wash, vary solids – Ratios for Figure 4</i>			
Unwashed stems	0.9	0.3	92.9
2 wt%-solids, 4h wash	1.3	32.8	88.0
4 wt%-solids, 4h wash	1.2	4.7	78.5
15 wt%-solids, 24h wash	2.4	3.3	84.2
16 wt%-solids, 4h wash	2.4	3.3	84.2
<i>4h, 4 % solids, 25 °C, stems, acid wash – Ratios for Figure 5</i>			
Unwashed stems	0.9	0.3	92.9
0 wt% H ₂ SO ₄	1.2	11.7	85.7
0.2 wt% H ₂ SO ₄	1.3	> 75 ^a	83.9
0.4 wt% H ₂ SO ₄	2.4	> 75	93.5
1.0 wt% H ₂ SO ₄	2.8	> 75	90.6
<i>24h, 10 % solids, 50 °C, whole straw, acid – Ratios for Figure 6</i>			
Unwashed whole straw	1.3	0.5	96.4
0 wt% H ₂ SO ₄	1.3	35.6	59.0
0.2 wt% H ₂ SO ₄	2.3	13.2	63.0
0.4 wt% H ₂ SO ₄	2.6	5.6	86.1
1.0 wt% H ₂ SO ₄	nd ^b	nd	nd

a Cl was not detected by EDS in this sample, so the approximate Cl detection limit was used to calculate the minimum possible SiO₂/KCl ratio.

b nd = not determined

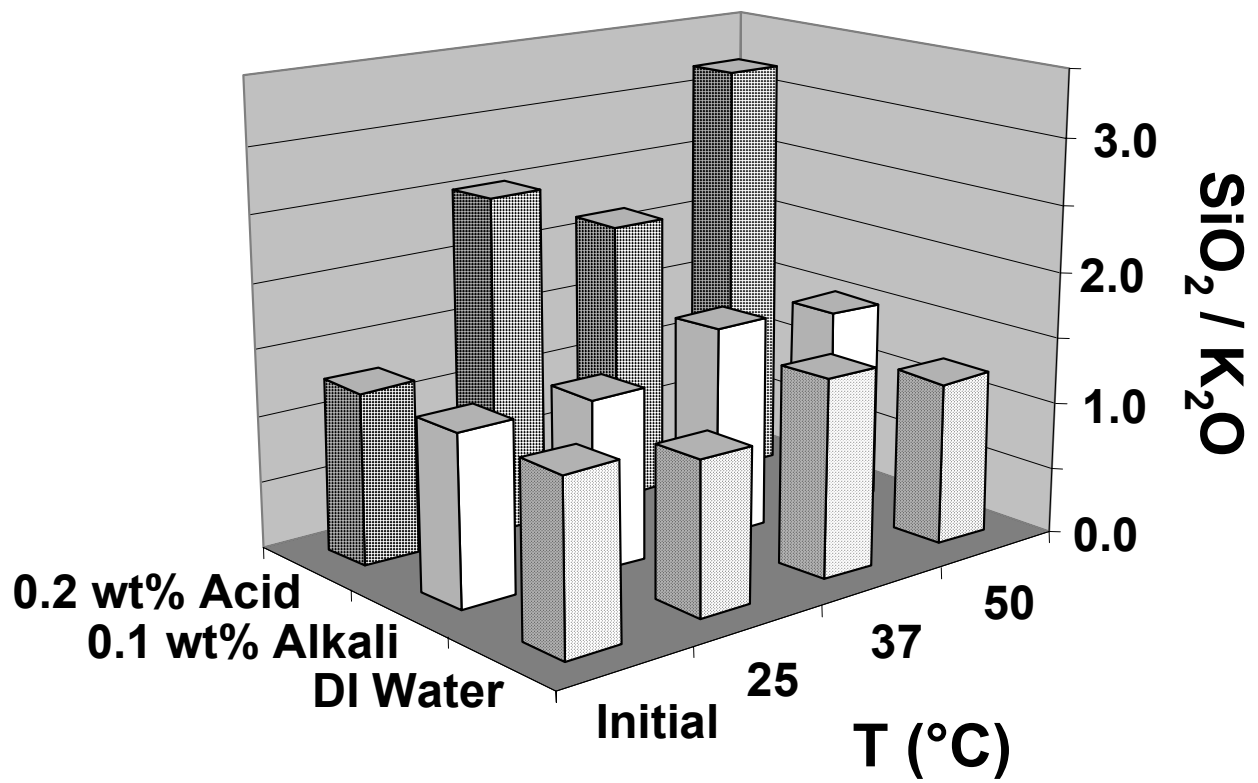


FIGURE 1 – Thompson, Shaw, and Lacey

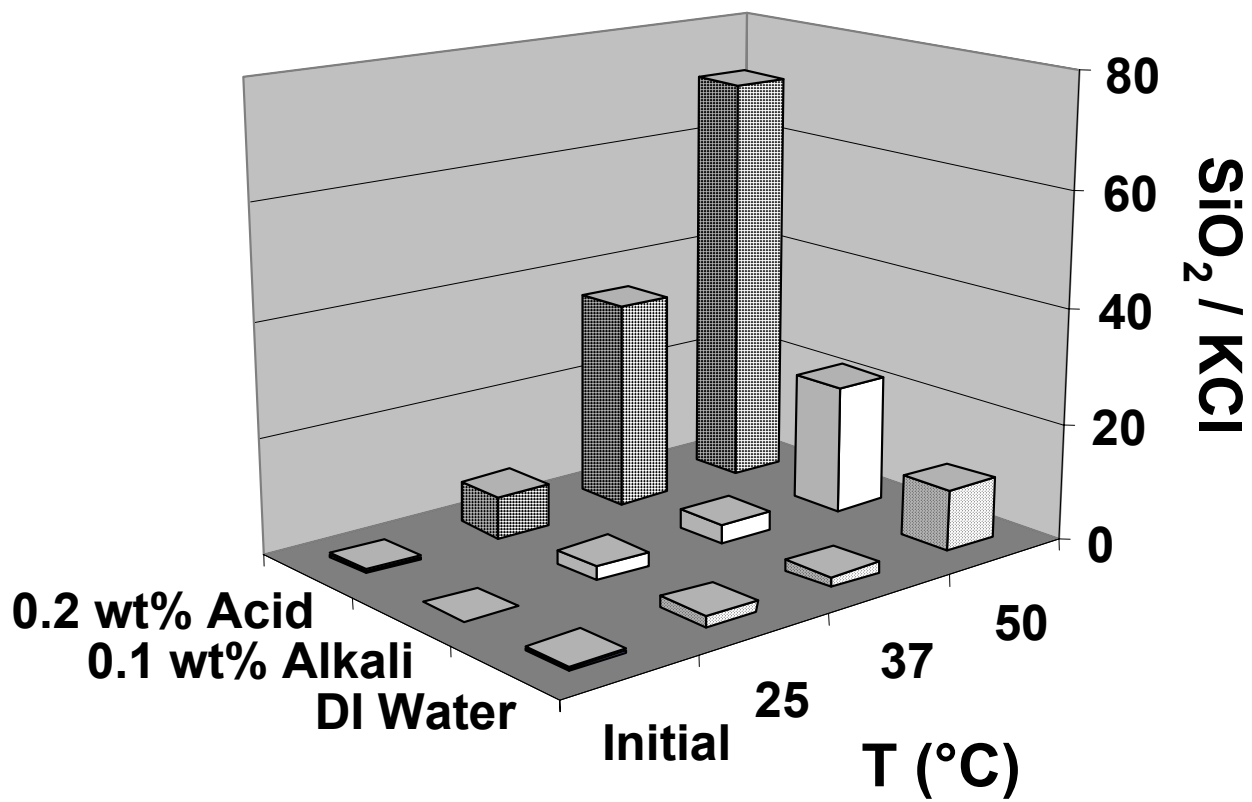


FIGURE 2 – Thompson, Shaw, and Lacey

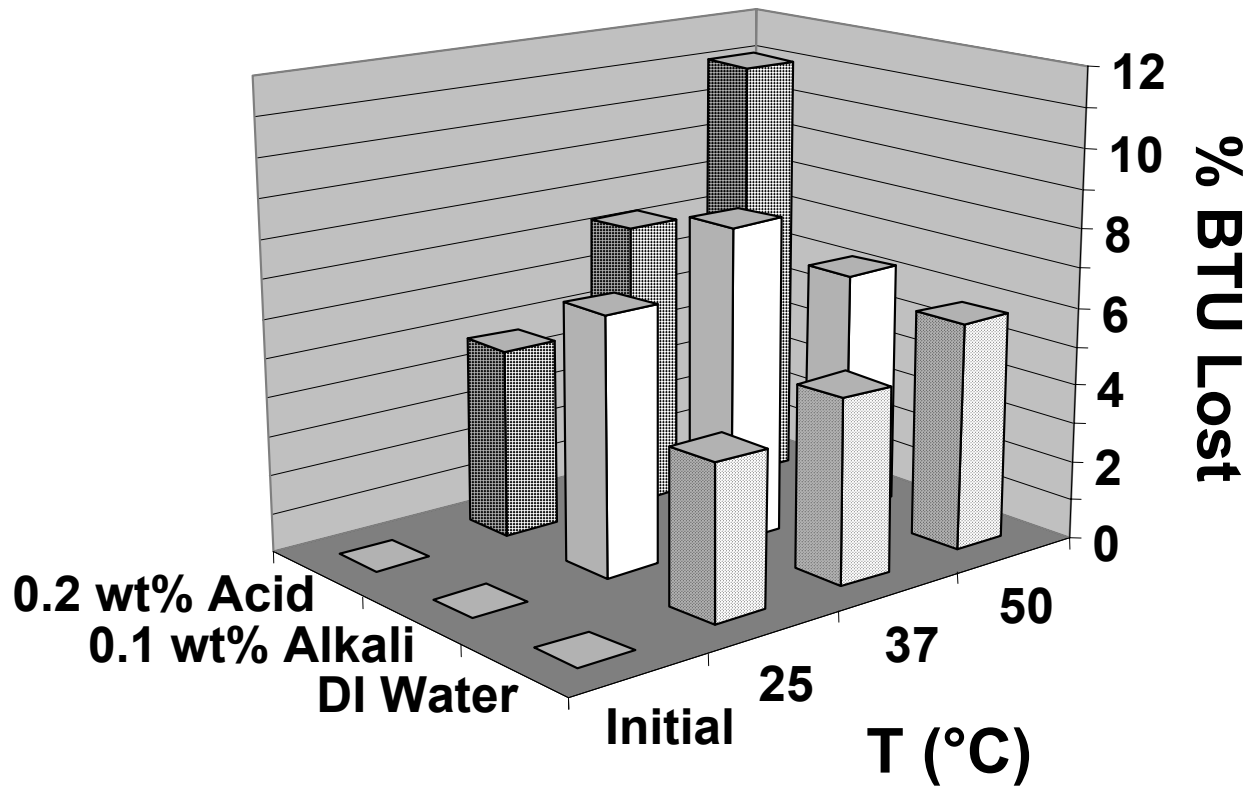


FIGURE 3 – Thompson, Shaw, and Lacey

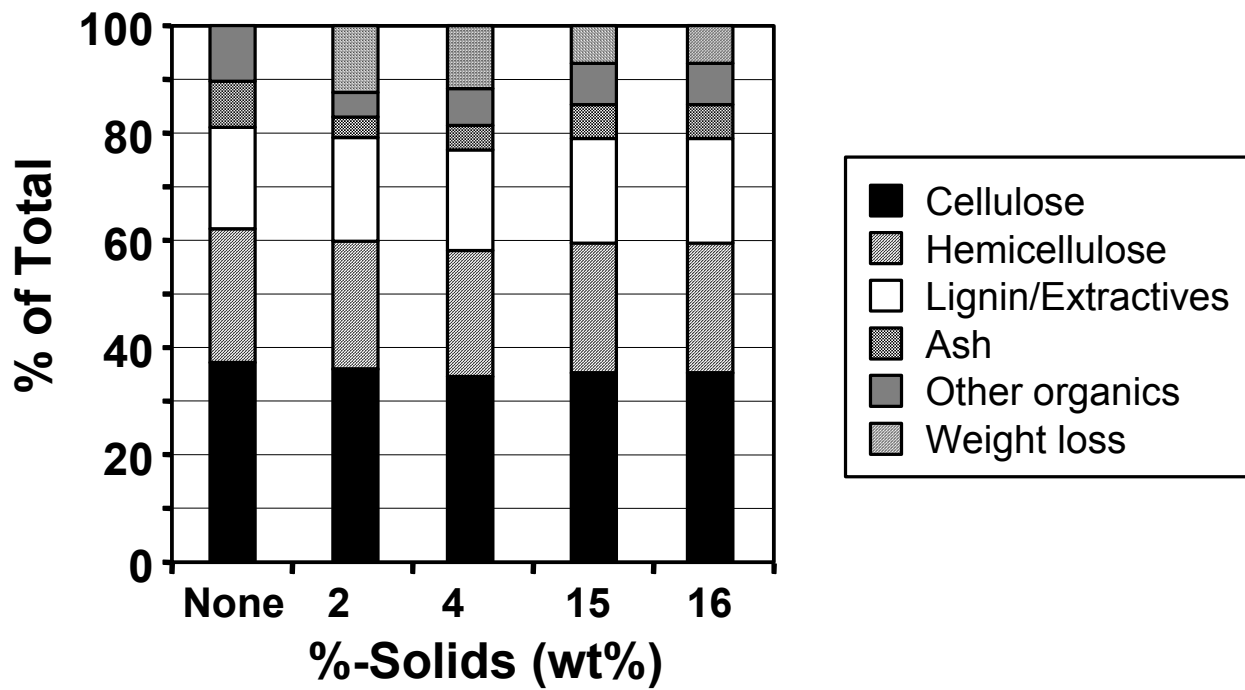


FIGURE 4 – Thompson, Shaw, and Lacey

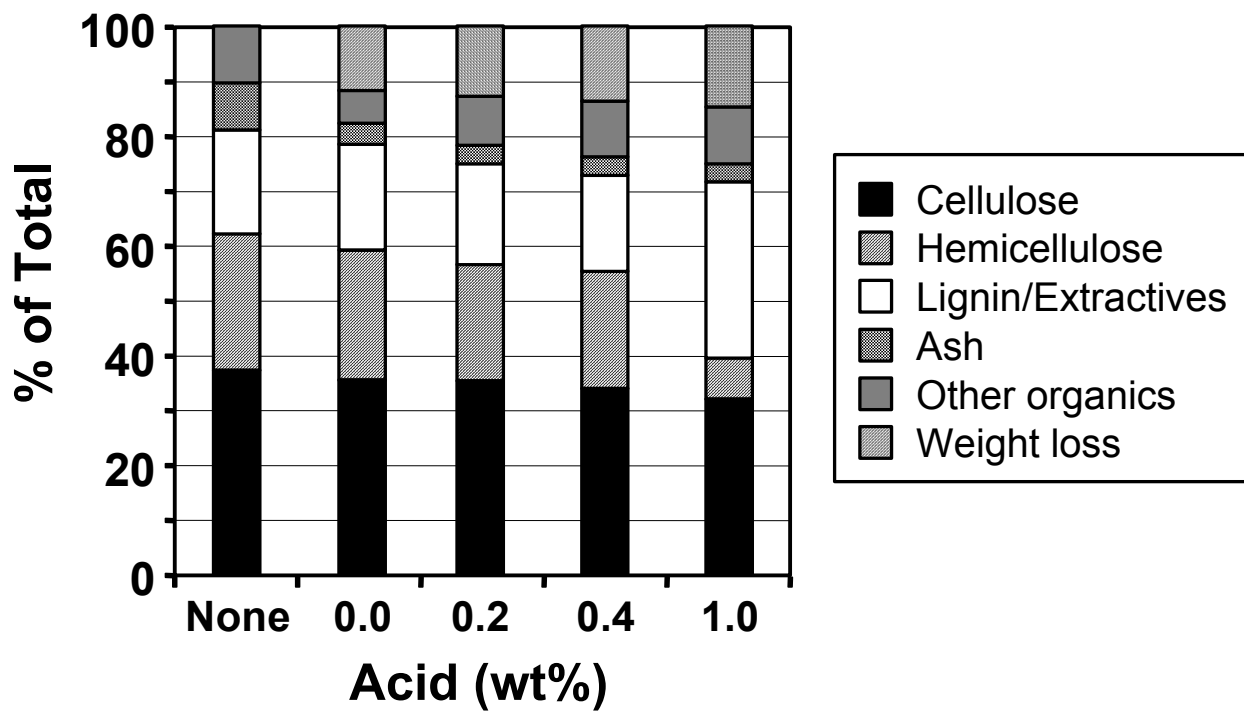


FIGURE 5 – Thompson, Shaw, and Lacey

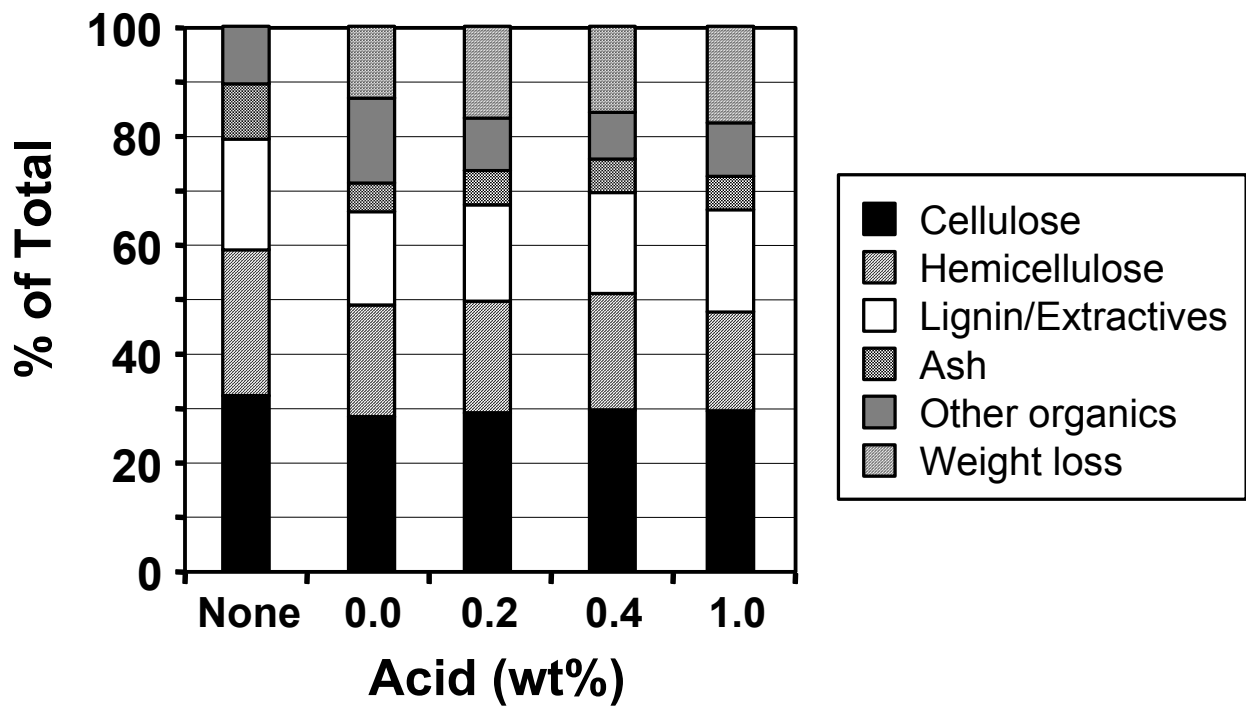


FIGURE 6 – Thompson, Shaw, and Lacey